

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Katsuhiko YAMANAKA, et al.

Serial No. Application of 10/736,682

Filed: December 17, 2003

For: FLAME-RESISTANT RESIN COMPOSITION AND ARTICLE

Hon. Commissioner of Patents and Trademarks
Washington, D.C. 20231

D E C L A R A T I O N

I, Katsuhiko YAMANAKA, am one of the inventors of U.S. Patent Application No. 10/736,682 and have thorough knowledge of the invention of this application.

I read the Official Action from the Examiner dated March 17, 2006. Then, I have conducted the following experiments to distinguish the invention of the present application from US 4162278 cited by the Examiner.

I. Outline of experiments

Experiment 1:

Sample C (dibenzyl pentaerythrityl diphosphonate) in Table 1 is used as a flame retardant in US 4162278.

This sample C was synthesized by the Arbuzov-type rearrangement process. Obtained compound is referred "Sample C."

Experiment 2:

Sample B (diphenyl pentaerythrityl diphosphonate) in Table 1 is used as a flame retardant in US 4162278.

Since this Sample B cannot be synthesized by the

Arbuzov-type rearrangement process, it was synthesized by the following method. Obtained Compound is referred "Sample B."

Experiment 3:

2,4,8,10-tetraoxa-3,9-diphosphaspyro [5.5] undecane, 3,9-dibenzyl-3,9-dioxide was synthesized by the same method of Preparation Example 7 of the present specification. Obtained compound is referred "Sample Z."

Experiment 4:

Sample C, Sample B and Sample Z synthesized in Experiments 1 to 3 were used as flame retardants and mixed with high-impact polystyrene (HIPS) to prepare flame retardant resin compositions so as to check their flame retarding effects.

II. Experiments

Experiment 1:

Preparation of

2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane,3,9-dibenzyl-3,9-dioxide:

22.55 g (0.055 mol) of 3,9-dibenzyl-3,9-dioxide, 19.01 g (0.11 mol) of benzyl bromide and 41.36 g (0.47 mol) of dioxane were charged into a reactor having a stirrer, thermometer and capacitor, and dry nitrogen was caused to flow while they were stirred at room temperature. Thereafter, the mixture was heated in an oil bath and stirred at a reflux temperature (about 100°C) for 4 hours. After the end of heating, the resulting solution was left to be cooled to room temperature, and 20 ml of dioxane was added to the solution and further stirred for 30 minutes. The precipitated crystals were separated by filtration, and the obtained filtrate was dried at 100°C and 1.33×10^2 Pa. The obtained white solid was confirmed to be 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane,3,9-dibenzyl-3,9-dioxide by ^1H , ^{31}P -NMR (^{31}P NMR purity was 85 %).

Experiment 2:

Preparation of

2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane,
3,9-diphenyl-3,9-dioxide:

54.5 g (0.4 mol) of dipentaerythritol, 3.2 g (0.04 mol) of pyridine and 400 ml of dioxane were charged into a reactor having a stirrer, thermometer and capacitor, and dry nitrogen was caused to flow while they were stirred at room temperature. Thereafter, 156.0 g (0.8 mol) of phenylphosphonic acid dichloride was added dropwise to the resulting solution and stirred at room temperature for 1 hour after the end of addition. Thereafter, the mixture was heated in an oil bath and stirred at about 50°C for 4 hours. After the end of heating, the resulting solution was left to be cooled to room temperature, the precipitated crystals were separated by filtration, and the obtained filtrate was dried at 100°C and 1.33×10^2 Pa. The obtained white solid was confirmed to be 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane, 3,9-diphenyl-3,9-dioxide by ^1H , ^{31}P -NMR (^{31}P NMR purity was 74 %).

Experiment 3:

6.81 Parts of pentaerythritol, 0.4 parts of pyridine and 80.0 parts of dioxide were charged into a reactor equipped with a thermometer, a condenser and a dropping funnel and stirred. Then, 19.5 parts of benzyldichlorophosphonic acid was added to the reactor by use of the dropping funnel. After completion of the addition, the mixture was refluxed under heating. After reacted, the mixture was cooled to room temperature, and obtained crystals were washed with water and methanol and then filtered. The crystals filtered out were dried at 120°C and 133 Pa for 3 hours to obtain 15.3 parts of a white solid. It was confirmed by ^{31}P , a ^1H NMR spectrum and measurement of a melting point that the obtained solid was a target 2,4,8,10-tetraoxa-3,9-diphosphaspyro [5,5] undecane, 3,9-dibenzyl-3,9-dioxide. The yield was 75%, and ^{31}P NMR purity was 99%.

Experiment 4:

The diposphonate compounds obtained by the above Experiments 1 to 3 were each blended with amounts (parts by weight) shown in the table below of components shown in the table below by a tumbler, the resulting blends were pelletized by a 15 mm-diameter double-screw extruder (KZW15 of Techno Bell Co., Ltd.) at a cylinder temperature of 220°C, and the obtained pellets were dried with a hot air drier heated at 70°C for 4 hours. The pellets were molded into test samples at a molding temperature of 210°C and a mold temperature of 40°C by an injection molding machine (J75Si of Nippon Steel Co., Ltd.). The evaluation results of these test samples are shown in the table below.

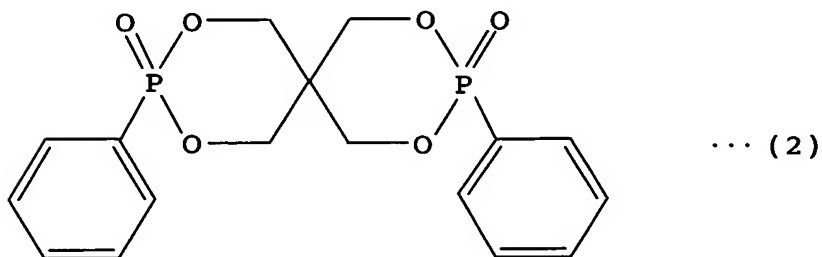
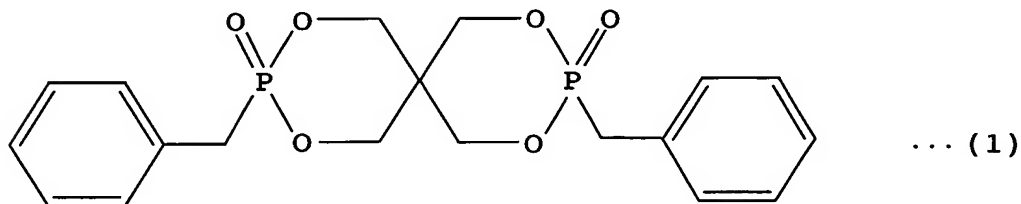
The measurements of flame retardancy UL-94, HDT and retention of HDT were carried out in accordance with the methods in the specification of the present application.

In the table, HIPS1 and HIPS2 are as follows.

HIPS1: Stylon 433 of A & M Styrene Co., Ltd.

HIPS2: Stylon 492R of A & M Styrene Co., Ltd.

Samples C and Z are compounds represented by the following formula (1) and Sample B is compound represented by the following formula (2).



		Unit	R.Ex. 1	R.Ex. 2	Ex. 1	Ex. 2	C.Ex. 1	C.Ex. 2	C.Ex. 3	C.Ex. 4
Kind of HIPS	HIPS1	Parts by weight	100	-	100	-	100	-	100	-
	HIPS2	Parts by weight	-	100	-	100	-	100	-	100
Kind of flame retardant	Sample Z	Parts by weight	-	-	5	15	-	-	-	-
	Sample C	Parts by weight	-	-	-	-	5	15	-	-
	Sample B	Parts by weight	-	-	-	-	-	-	5	15
Evaluation of results	Flame retardancy UL-94 (3.2mm)		not V	not V	V-2	V-2	not V	not V	not V	not V
	Flame retardancy UL-94 (1.6mm)		not V	not V	V-2	V-2	not V	not V	not V	not V
	HDT	°C	70.7	79.4	70.4	78.3	66.0	71.1	64.5	70.9
	Retention of HDT	%	-	-	99.6	98.6	93.4	89.5	91.2	89.3

R.Ex: Referential Example

Ex. Example

C.Ex.: Comparative Example

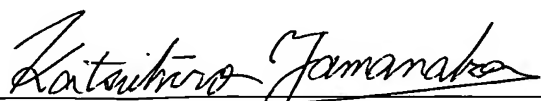
III. Considerations

The following can be understood from the above table.

- (a) When the high-purity Sample Z obtained Experiment 3 is used to flame retard HIPS, V-2 level is achieved and the high retention of HDT is obtained (see Examples 1 and 2).
- (b) In contrast to this, when the low-purity Sample C obtained in Experiment 1 is used as a flame retardant, V level is not achieved. In addition to this, the retention of HDT greatly worsens (see Comparative Examples 1 and 2).
- (c) Further, when the low-purity Sample B obtained in Experiment 2 is used as a flame retardant, V level is not achieved. In addition, the retention of HDT greatly worsens (see Comparative Examples 3 and 4).
- (d) It can be understood from the above that the high-purity Sample Z is used to flame retard HIPS, V-2 flame retardancy sample Z is achieved and the high retention of HDT is obtained.

The undersigned declarant further declares that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

The 30th of June, 2006



Katsuhiro YAMANAKA